



Technical note

## The use of a porous ceramic diaphragm for the removal of metallic impurities from chromium plating baths

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### 1. Introduction

The 'porous pot' has been used in the plating industry and can be classified as an electrolytic separation technique [1–3]. Compared with other separation techniques, there are several advantages in using a porous ceramic diaphragm to separate metal impurities from plating solutions. Theoretically, metallic impurities from the plating solutions accumulate inside the ceramic pot and can either be precipitated as sludge or deposited onto the cathode. Concurrently, Cr(III) may be oxidized to Cr(VI) at the anode in the plating bath solution, thereby keeping its concentration low. An advantage of the porous pot is that it can be operated concurrently with the plating process, thereby allowing semi-continuous removal of metallic impurities and oxidation of Cr(III). This is desirable since the presence of high concentrations of Cr(III) in the plating bath causes surface roughness of the hard-chromium deposit and reduces current efficiency.

Among previous investigators, Mandich [2, 3] claimed the 'porous-pot method' to be the most cost-efficient process to separate impurities from the plating solution, at least for relatively small operations. Cushnie and Anderson [1] considered its separation efficiency to be marginal.

The porous ceramic material is a stable and relatively inexpensive diaphragm, compared to ion-exchange resins, electrodialysis membranes, and semi-permeable polymer membranes. These types of membranes are usually not resistant to hot chromic acid, and can only be used with dilute solutions (e.g., rinse tanks or diluted baths) [4].

Even though the ceramic pot method may be an economical device for removing metallic impurities and simultaneously reoxidizing chromium(III), its operation remains poorly understood. Mandich [2, 3] described the mode of operation in detail and for the first time suggested a qualitative explanation of the reactions taking place. According to Mandich [2], when a potential of about 5 ~ 6 V is applied, most of the Cr(III) in the main bath is reoxidized at the anode and a small fraction of Cr(III) migrates to the catholyte through the diaphragm.

Metallic impurities such as Fe<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> also migrate through the diaphragm to the cathode compartment. Protons or H<sub>2</sub>O are reduced at the cathode and hydrogen evolution occurs, raising the pH of the catholyte. As the concentration of hydroxyl ion (OH<sup>-</sup>) increases inside the ceramic pot, metal hydroxides precipitate in the catholyte chamber (in the 'porous pot').

The aim of this research project was to quantitatively analyse the 'porous pot process' using a reduced-scale cell containing a porous ceramic diaphragm. The experiments were designed to reproduce real-world plating conditions as closely as possible.

### 2. Experimental details

A contaminated chromium plating solution similar to one used in plating practice was made with a chromic acid concentration of approximately 2.5 M (250 g L<sup>-1</sup>), 0.025 M (2.5 g L<sup>-1</sup>) H<sub>2</sub>SO<sub>4</sub>, and Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup> and Ni<sup>2+</sup> as impurities [1, 4]. These impurities were added in the form of sulfates (FeSO<sub>4</sub>·7 H<sub>2</sub>O, CuSO<sub>4</sub>, NiSO<sub>4</sub>·6 H<sub>2</sub>O and Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·12 H<sub>2</sub>O) to achieve impurity concentrations in the range of 25 to 250 mM (2–15 g L<sup>-1</sup>). Barium carbonate (BaCO<sub>3</sub>) was used to eliminate excess sulfate anion by the formation of a water-insoluble precipitate (BaSO<sub>4</sub>). Filters were used to separate the BaSO<sub>4</sub> precipitate from the plating solution.

A lab-scale porous pot cell was designed and fabricated [5] using a rectangular piece of ceramic (proprietary material containing primarily Mg, Al and Si) made by Hard Chrome Plating Consultants Inc., Cleveland, OH. The ceramic piece was 0.625 cm thick by 6.5 cm × 8 cm with a porosity of 40%, and a mean pore size of approximately 1 μm. To prepare a model-test cell, a 250 mL glass beaker was sectioned along its height at the centre into symmetrical halves. The flat end of the half cell was then closed with a sheet of ceramic and sealed with silicon rubber. A schematic of the lab-scale porous pot is shown in Figure 1.

A lead plate cathode having dimensions of 2.5 cm × 2.0 cm × 0.1 cm was used in the first set of

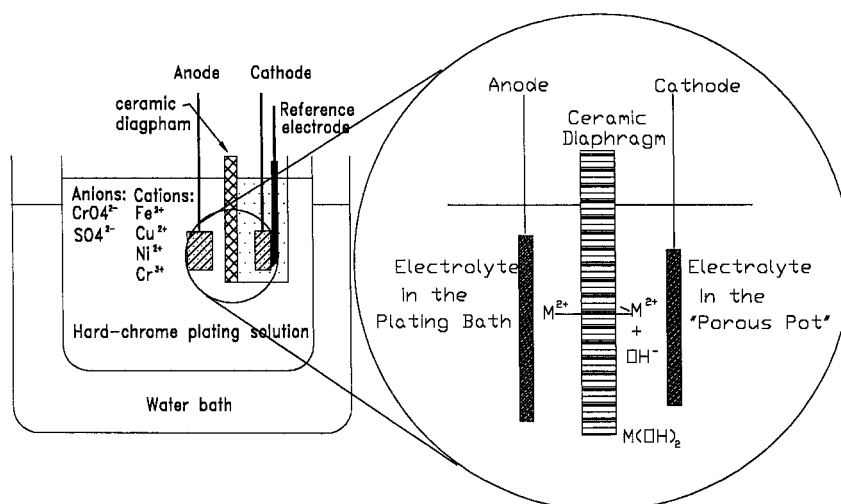


Fig. 1. Schematic diagram of the porous pot purification system (adapted from [5]).

experiments. In the second set of experiments a lead grid cathode ( $3\text{ cm} \times 3\text{ cm} \times 0.5\text{ cm}$ ) with approximately 50% open area was used. A lead grid anode ( $4\text{ cm} \times 4\text{ cm} \times 0.5\text{ cm}$ ) was suspended in the bulk plating solution close to the ceramic diaphragm in all of the experiments. A mercury-mercurous sulfate reference electrode ( $\text{Hg}/\text{Hg}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ (saturated),  $V = 0.64\text{ V}$  vs NHE) was used to measure the potential difference between the reference electrode and the cathode. This lab-scale cell was suspended inside a 7 L tank holding the chromium plating solution (Figure 1).

The applied current was generated with a Hewlett Packard DC power supply (HP 6632A). The cell potential and cathode/reference electrode potential were recorded and stored in a digital oscilloscope (Nicolet 310). The pH was monitored with an Orion pH meter (model 620) and combination electrode. The amount of  $\text{CrO}_3$  and  $\text{Cr}^{3+}$  was determined using titration [5]. The concentrations of iron, copper and nickel were determined by atomic absorption spectrometry (Perkin Elmer, model 460:060-0051).

Constant currents of 0.66, 0.34 and 0.25 A were used in the first set of experiments (lead plate cathode). The second set of experiments (lead grid cathode) were carried out at current levels of 0.37 and 1.0 A.

### 3. Experimental results

Six experiments were conducted as part of this research project (Table 1). In all of the experiments a slow fine

bubbling was seen at the anode immediately after applying the current, indicating oxygen evolution. The concentration of all of the metals in the plating solution decreased at a constant rate throughout each experiment (see Figure 2 for the results of experiment 1, with a flat lead cathode at 0.66 A). The pH of the plating solution generally decreased slightly and the pH of the solution in the porous pot increased. After operation for several hours the metal concentrations in the catholyte reached a high enough level for metal ion reduction reactions to become significant, and a thick gelatinous layer formed on the cathode (particularly in the high applied current experiments). This layer was nonporous and poorly conductive, thus sharply increasing the overpotential. At the end of the experiments a thick, very dark green layer was seen on the cathode, which was difficult to remove. The catholyte became viscous and some precipitate settled to the bottom of the porous pot.

## 4. Discussion

### 4.1. Effect of impurity concentration

The experiments showed that the higher the concentration of the impurity in the plating solution, the higher the removal rate (Table 2). For example, in experiment 1, the initial concentrations of Fe, Ni and Cu in the spent plating solution were 125 mM ( $7.0\text{ g L}^{-1}$ ), 81 mM ( $4.8\text{ g L}^{-1}$ ) and 26 mM ( $1.7\text{ g L}^{-1}$ ) and they were removed at a rate of  $0.93\text{ mm h}^{-1}$  ( $0.052\text{ g L}^{-1}\text{ h}^{-1}$ ),

Table 1. Calculated current density conditions for porous pot operations

Expt.	Cathode Material /Structure	Cathode dimensions / $\text{cm}^2$	Appl. current /A	Initial cell Voltage drop /V	$I_{\text{anode}}$ / $\text{A cm}^{-2}$	$I_{\text{cathode}}$ / $\text{A cm}^{-2}$
1	Lead plate cathode	$2.5 \times 2.5$	0.660	5.1	0.016	0.106
2	Lead plate cathode	$2.5 \times 2.5$	0.344	4.3	0.022	0.055
3,4	Lead plate cathode	$2.5 \times 2.5$	0.250	3.6	0.016	0.040
5	Lead grid cathode	$3.0 \times 3.0$	0.100	7.5	0.063	0.111
6	Lead grid cathode	$3.0 \times 3.0$	0.370	4.8	0.023	0.041

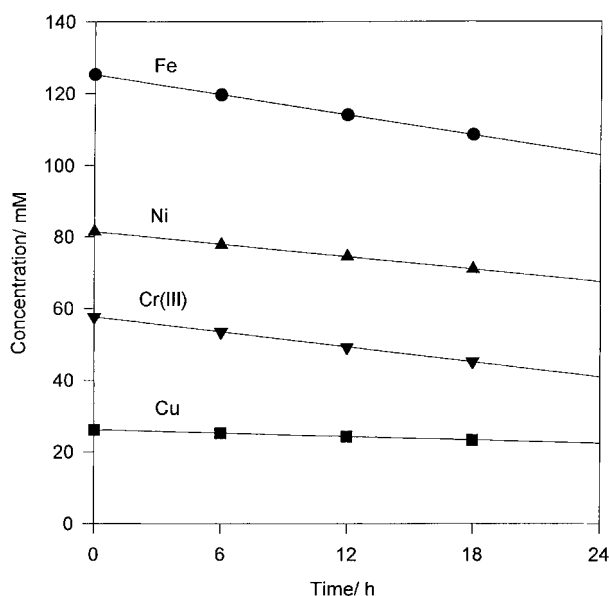


Fig. 2. Change in metal impurity concentration in the bulk plating solution with time (lead plate cathode at 0.66 A).

$0.58 \text{ mm h}^{-1}$  ( $0.034 \text{ g L}^{-1} \text{ h}^{-1}$ ) and  $0.16 \text{ mm h}^{-1}$  ( $0.01 \text{ g L}^{-1} \text{ h}^{-1}$ ), respectively. The higher removal rates for Cr(III) in experiments 5 and 6 compared to Cu which was at a similar concentration may be due to a trivalent ion being removed at a faster rate than divalent ions. However, it is likely that some of the Cr(III) was also oxidized to Cr(VI) at the anode, thereby increasing its removal rate.

#### 4.2. Effect of current

The removal rate was also a function of the current density at which the cell is operated. The higher the current density, the higher the removal rate (Table 2). For example, about  $0.93 \text{ mm h}^{-1}$  ( $0.052 \text{ g L}^{-1} \text{ h}^{-1}$ ) and  $0.58 \text{ mm h}^{-1}$  ( $0.034 \text{ g L}^{-1} \text{ h}^{-1}$ ) of Fe and Ni, respectively, were removed at 0.66 A operation whereas about  $0.50 \text{ mm h}^{-1}$  ( $0.029 \text{ g L}^{-1} \text{ h}^{-1}$ ) and  $0.28 \text{ mm h}^{-1}$  ( $0.019 \text{ g L}^{-1} \text{ h}^{-1}$ ) of Fe and Ni were removed at 0.25 A operation using a lead plate cathode.

Experiments 5 and 6 were carried out using a Pb grid electrode of approximately 50% open area with the same initial concentrations of the impurities, however the applied current in experiment 6 was approximately 1/3 of that in experiment 5. Correspondingly, the

removal rate of all of the cations was approximately 50% lower at the lower applied current (Table 2). However at the lower current, the cell operated continuously for 84 h whereas at the higher current the cell could only be operated for 6 h before cleaning. The reason for this will be discussed in the next section.

At 0.37 A, the hydroxide coating on the cathode was less thick and was easily removed. At both 0.37 and 0.25 A the pH of the catholyte increased continuously and most of the impurities were removed by precipitation and accumulation at the bottom of the porous pot.

#### 4.3 Optimum current density

High impurity removal rates can be achieved at high current densities. The disadvantage of high current densities is that the porous pot cannot be operated continuously because high current densities at the diaphragm and at the cathode cause adhesion of the hydroxide as a gel to the diaphragm or cathode or both. This necessitates frequent cleaning of the pot and the cathode. The type of precipitation depends on the area and roughness of the lead cathode as well as the current density. Low current densities cause precipitation and favour the operation of the porous pot on a continuous basis. However, at low current densities, the impurities will be removed at a slower rate and hence it may be difficult to maintain suitable bath conditions for plating.

Using a Pb grid electrode, the ceramic diaphragm cell can be operated continuously for much longer time with fewer interruptions. When a Pb grid cathode was used, the catholyte reached pH values as high as 13. Since the cathode is a grid, the effective cathodic current density is much less than the apparent current density. In spite of the formation of a thick metallic layer on the outside of the cathode, the active surface area available is high enough to allow hydrogen evolution to occur on a continuous basis, which increases the local pH of the catholyte. Due to this high pH, hydroxide precipitation reactions become dominant during the later period of operation.

The removal rate of impurities is expected to depend strongly on the ratio of the permeable surface area of the ceramic diaphragm to the volume of spent plating solution. If the flux of impurity ions through the diaphragm is rate controlled by the electric field the

Table 2. Initial concentrations and removal rates of various impurities from plating solution under different experimental conditions

Expt.	Appl. current /A	Initial concentration/mM				Removal rate/mM h <sup>-1</sup>			
		Fe	Cu	Ni	Cr(III)	Fe	Cu	Ni	Cr(III)
1	0.660	125	26	81	92	0.93	0.16	0.58	—
2	0.344	94	20	64	73	0.29	0.055	0.26	—
3	0.250	143	29	89	100	0.50	0.11	0.28	0.19
4	0.250	119	24	76	86	0.52	0.11	0.34	0.27
5	1.000	269	189	170	192	0.60	0.56	0.57	0.64
6	0.370	269	189	170	192	0.32	0.29	0.32	0.36

higher the area/volume ratio at fixed current the faster the removal rate. The lab-scale porous pot used in these experiments had a projected ceramic diaphragm area of 12.25 cm<sup>2</sup> and a permeable superficial area of 4.9 cm<sup>2</sup> (projected area  $\times$  porosity). Since the pot was operated with 5 L of plating solution, the projected area/volume ratio was about 0.0025 cm<sup>-1</sup>. Based on this ratio, plating tanks having volumes of 55 gallons (200 L) and 3000 gallons (11 m<sup>3</sup>) require about 0.05 and 2.75 m<sup>2</sup> projected diaphragm surface area, respectively, to obtain similar removal rates.

From data reported for commercial porous pots [2, 3, 6] a maximum current density of 0.05 A cm<sup>-2</sup> of ceramic area should be used during porous pot operation. According to our results, the applied current density should be less than this to minimize interruptions for cleaning and sludge removal. The optimum current density is in the range 0.01–0.03 A cm<sup>-2</sup>. For example, the optimum current for a 200 L (55 gal) purification tank, based on experimental area to volume ratios, is about 5 ~ 10 A. This value would apply to systems similar to those used in these experiments with respect to diaphragm porosity and the type of cathode used.

## 5. Conclusions

The results of this research confirm that the porous pot method is an effective method to separate impurities from, and recycle chromium to, plating solutions. The most important practical conclusions (see also reference [6]) are: (i) that high impurity removal rates can be achieved at high current densities. The disadvantage of such relatively high current densities is that frequent cleaning of the pot as well as the cathode is required; and (ii) that a lead grid cathode of approximately 50% open area works better than a lead plate electrode

because fewer interruptions for cleaning are required. Using the lead grid cathode the bulk catholyte reached very high pH values (up to 13) and the impurities precipitated as a compact sludge. When a lead plate electrode was used as the cathode, the impurities were coated onto the cathode as an adherent layer.

Fundamentally, our results are in agreement with the assumption that the potential gradient across the diaphragm and, therefore, the ratio of ceramic diaphragm area to the volume of spent solution determines the impurity removal rate from the plating solution.

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